

Solubility in Water and Phase Partitioning of Highly Hydrophobic Organic Solutes at Environmental Conditions

V. Majer^{C.S}

Laboratoire de Thermodynamique des Solutions et des Polymères, UMR 6003 CNRS, Université Blaise Pascal, Aubière, France

G. Bergin

UMR 6003 CNRS /Laboratoire de Thermodynamique des Solutions et des Polymères, Université Blaise Pascal, Aubière, France

J. Sedlbauer

Department of Chemistry, Technical University of Liberec, Liberec, Czech Republic

M.F. Costa-Gomes

Laboratoire de Thermodynamique des Solutions et des Polymères UMR 6003 CNRS, Université Blaise Pascal, Aubière, France

Hydrophobe organic substances such as hydrocarbons and their derivatives of low polarity are considered as environmental chemicals for their negative impact on biota. Many of them are high molar mass compounds of low volatility and water solubility limiting considerably their transport between different compartments of the environment. Nevertheless an important part of these chemicals are highly stable with a possibility of gradual accumulation in plants and in living organisms with a subsequent food chain transport and biomagnification. Thermodynamic data allowing phase equilibrium calculations are therefore crucial for evaluating the extent of the environmental impact and also for developing depollution processes. Of major importance is particularly the correct expression of the fugacity of solutes in an aqueous phase which is the main spread vector of these organic contaminants. Beside solubility in water and vapor pressures, thermal data are also needed, especially for calculations with solutes which are solid at ambient conditions. Establishing prediction schemes requires knowledge of reliable data for the key chemical structures which are missing for many heavy organic solutes due to difficulty of their experimental determination. After a brief thermodynamic introduction three topics will be addressed in this review lecture. Firstly the availability of experimental data on solubility of hydrocarbons will be discussed and major experimental approaches to their determination will be outlined. Attention will be paid to the saturation column method which is particularly adapted for determination of extremely low solubilities (down to $x_{\text{sol}} \sim 10^{-10}$). Secondly ways of predicting parameters necessary for fugacity calculation such as the limiting activity coefficients and the Henry's law constants will be shown. The concept of hydration properties as a basis of a prediction scheme will be presented as an alternative to empirical correlations prevailing in environmental science. Finally the necessity to improve knowledge of aqueous polyaromatic hydrocarbons will be documented by the data on aqueous solubilities which are scanty and non consistent. Indications will be given for additional experimental work needed to describe this major class of environmental chemicals and to allow the development of predictions for polycyclic hydrocarbons and their heterogeneous derivatives.